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(54) High Temperature Resistant Foams

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HIGH TEMPERATURE RESISTANT FOAMS

ABSTRACT OF THE DISCLOSURE

The invention relates to high temperature resistant foams prepared by partially reacting an organic polyisocyanate with an epoxide having at least two epoxide groups in quantities such that the equivalent ratio of isocyanate groups to epoxide groups is from 1.2:1 to 500:1 in the presence of a tertiary amine catalyst; adding an alkylating sulfonic acid alkyl ester, methyl iodide, or dimethyl sulfate to terminate the reaction when no more than about 60% of the isocyanate groups have reacted; and foaming the resultant stable intermediate mixture by adding a chemical and/or physical blowing agent and a catalyst that accelerates the reaction of isocyanate and epoxide groups.

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HIGH TEMPERATURE RESISTANT FOAMSBACKGROUND OF THE INVENTION

The present invention relates to high temperature
5 resistant foams obtainable by the reaction of a reaction
mixture ("A-state") of organic polyisocyanates, organic
polyepoxides, special catalysts, and reaction stoppers to form
10 a storage-stable, more highly viscous intermediate "B-state"
and the conversion of this more highly viscous B-state into the
foamed, non-fusible final "C-state" by the addition of chemical
and/or physical blowing agents and a catalyst that
15 spontaneously accelerates the isocyanate-epoxide reaction
without the application of heat.

According to European Patent Application 272,563,
15 molded articles can be produced in two stages by the conversion
of a storage stable B-state by the addition of heat-activated
latent catalysts. The reference suggests that resins in the
"B-state" could conceivably be used in combination with
suitable blowing agents for the production of foams. The
20 reference, however, does not suggest how this foaming process
should be, or, in fact, must be carried out, because resins
according to EP 272,563 are converted into the final
cross-linked state by being heated.

It is evident from European Patent Application
25 296,052 that high temperature resistant foam may be obtained
from mixtures of diisocyanates and bis-epoxides in the presence
of porous expanded or dispersed materials. Without the
addition of porous particles, the specified starting mixtures
cannot be worked up into a foam.

30 It is an object of the present invention to provide
high temperature resistant foams that can be prepared by a
simple process and will harden without the application of heat,
thereby enabling production of such foams under industrial
conditions with short residence times in the molds.

SUMMARY OF THE INVENTION

The invention relates to high temperature resistant foams prepared by a process comprising

- (1) reacting a mixture of

5 (a) at least one organic polyisocyanate with
(b) at least one organic compound containing at least two epoxide groups in a quantity corresponding to an equivalent ratio of isocyanate groups to epoxide groups of from about 1.2:1 to about 500:1,

10 in the presence of

(c) a tertiary amine as catalyst,
thereby forming an intermediate containing oxazolidinone and/or isocyanurate groups;

- (2) terminating step (1) when no more than about 60%

15 (preferably 10% to 30%) of the isocyanate groups of component (a) have reacted by adding at least an equivalent amount, based on the tertiary amine (c), of
(d) an alkylating sulfonic acid alkyl ester, methyl iodide, or dimethyl sulfate,

20 thereby forming a stable B-state intermediate having a viscosity of from 1500 to 20,000 mPa·s at 25°C; and

- (3) converting said B-state intermediate to the high temperature resistant foam by adding

25 (e) chemical and/or physical blowing agents and
(f) a catalyst for accelerating reaction of isocyanate and epoxide groups.

The invention further relates to the process for preparing the high temperature resistant foams according to the invention.

30 DETAILED DESCRIPTION OF THE INVENTION

In a preferred embodiment, the invention relates to the preparation of high temperature resistant foams in which the chemical blowing agents (e) are water and/or phospholine oxide, the physical blowing agents (e) are low boiling inert organic liquids, and the catalysts (f) are tertiary amines

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5 (preferably pentamethyl diethylenetriamine). It was extremely surprising to find, and not foreseeable to one skilled in the art, that high temperature resistant foams could be obtained by the process according to the invention with such a wide variety of blowing agents.

10 The invention also relates to a process in which other known auxiliary agents and additives (g) are incorporated into one or more of components (a), (b), (c), (d), and (f). In a preferred embodiment, the invention relates to a process for the preparation of high temperature resistant foams in which the auxiliary agents and additives (g) are foam stabilizers, mold release agents, and dyes in a maximum quantity of up to about 10% by weight, based on the total weight of components (a) and (b) (excluding the quantity of any auxiliaries and additives added to (a) or (b)), and inorganic and/or organic fillers, olefinically unsaturated compounds (in particular, styrene and/or maleimide derivatives), and/or organic compounds in the molecular weight range of from about 62 to about 8000 containing at least two alcoholic hydroxyl groups in a quantity of up to about 100% by weight, based on the total weight of components (a) and (b) (excluding the quantity of any auxiliaries and additives added to (a) or (b)).

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20 The starting components (a) may be any of the organic polyisocyanates known to be useful in polyurethane chemistry, such as the aliphatic, cycloaliphatic, araliphatic, aromatic, and heterocyclic polyisocyanates described by W. Siefken in Justus Liebigs Annalen der Chemie, 562, pages 75 to 136. Examples of suitable polyisocyanates include those of the formula $Q(NCO)_n$ wherein n is 2-4 (preferably 2) and Q is an aliphatic hydrocarbon group having 2-18 (preferably 6-10) carbon atoms, an aromatic hydrocarbon group having 6-15 (preferably 6-13) carbon atoms, or an araliphatic hydrocarbon group having 8-15 (preferably 8-13) carbon atoms, such as ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate,

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cyclobutane-1,3-diisocyanate, cyclohexane-1,3- and -1,4-di-isocyanate and any mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane (German Auslegeschrift 1,202,785 and U.S. Patent 3,401,190), 2,4- and 5 2,6-hexahydrotoluene diisocyanate and any mixtures of these isomers, hexahydro-1,3- and/or -1,4-phenylene diisocyanate, perhydro-2,4'- and/or -4,4'-diphenylmethane diisocyanate, 1,3- and 1,4-phenylene diisocyanate and 2,4- and 2,6-toluene diisocyanate and any mixtures of these isomers, diphenyl-10 methane-2,4- and/or -4,4'-diisocyanate, and naphthylene-1,4-diisocyanate.

Other suitable polyisocyanates include triphenyl-methane-4,4',4"-triisocyanate, polyphenyl-polynaphthalene polyisocyanates obtainable by aniline-formaldehyde condensation followed by phosgenation (British Patents 874,430 and 848,671) 15 m- and p-isocyanatophenylsulfonyl isocyanates (U.S. Patent 3,454,606), perchlorinated aryl polyisocyanates (U.S. Patent 3,277,138), polyisocyanates containing carbodiimide groups (U.S. Patent 3,152,162), norbornane diisocyanates (U.S. Patent 3,492,330), polyisocyanates containing allophanate groups (British Patent 994,890), polyisocyanates containing isocyanurate groups (U.S. Patent 3,001,973), polyisocyanates containing urethane groups (U.S. Patents 3,394,164 and 3,644,457), polyisocyanates containing acylated urea groups 20 (German Patentschrift 1,230,778), polyisocyanates containing biuret groups (U.S. Patents 3,124,605, 3,201,372, and 3,124,605), polyisocyanates prepared by trimerization reactions (U.S. Patent 3,654,106), polyisocyanates containing ester groups (U.S. Patent 3,567,763), reaction products of the above-mentioned isocyanates with acetals (German Patentschrift 30 1,072,385), and polyisocyanates containing polymeric fatty acid esters (U.S. Patent 3,455,883). It is also possible to use distillation residues containing isocyanate groups from the commercial production of isocyanates, optionally dissolved in 35 one or more of the above-mentioned polyisocyanates. Any

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mixtures of the above-mentioned polyisocyanates may also be used.

It is generally preferred to use commercially available polyisocyanates such as 2,4- and 2,6-toluene diisocyanate and any mixtures of these isomers ("TDI"); preferably, polyphenyl-polymethylene polyisocyanates which may be prepared by aniline-formaldehyde condensation followed by phosgenation ("crude MDI"); and polyisocyanates containing carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups, or biuret groups ("modified polyisocyanates"), particularly modified polyisocyanates derived from 2,4- and/or 2,6-toluene diisocyanate or from 4,4'-and/or 2,4'-diphenylmethane diisocyanate.

An isomeric and/or homologous mixture of polyisocyanates of the diphenylmethane series containing more than about 20% by weight of 2,4'-diisocyanatodiphenylmethane is particularly preferred. These mixtures are polyisocyanate mixtures of the diphenylmethane series containing more than about 20% by weight (preferably from 30 to 70% by weight) of 2,4'-diisocyanatodiphenylmethane. In addition to these 2,4'-isomers, the particularly preferred polyisocyanate component generally contains other isomeric or homologous polyisocyanates of the diphenylmethane series. Thus, the particularly preferred polyisocyanate component generally contains mixtures of 2,4'-diisocyanatodiphenylmethane and 4,4'-diisocyanatodiphenylmethane and up to about 20% by weight, based on the total mixture, of 2,2'-diisocyanatodiphenylmethane or mixtures of these isomers with higher nuclear polyphenyl-polymethylene polyisocyanates. Mixtures containing higher nuclear polyphenyl-polymethylene polyisocyanates generally contain from about 10 to about 60% by weight, based on the total mixture, of such higher nuclear polyisocyanates. The diisocyanate mixtures enriched with 2,4'-isomers, which may be used as a preferred polyisocyanate component, may be obtained, for example, by distilling a diisocyanate mixture of the

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composition described above from a polyisocyanate mixture obtained by the phosgenation of a product of aniline-formaldehyde condensation. The mixture containing higher nuclear polyisocyanates, which is also a particularly preferred mixture, may be obtained, for example, by back-mixing a distillation product with a phosgenation product that has been depleted of 4,4'-diisocyanatodiphenylmethane, for example, according to German Auslegeschrift 1,923,214. Such a mixture, that is, a polyisocyanate mixture containing 2,4'-diisocyanato-diphenylmethane in the proportions indicated above, may also be obtained directly by suitably controlling the aniline-formaldehyde condensation process. U.S. Patent 3,277,173, for example, describes a method for obtaining polyamine mixtures of the diphenylmethane series containing a high proportion of 2,4'-diaminodiphenylmethane. The particularly preferred polyisocyanates may then be obtained by phosgenating such condensates having a high 2,4'-diaminodiphenylmethane content. Methods of obtaining such polyisocyanate mixtures are also mentioned in German Offenlegungsschrift 1,937,685 and in U.S. Patent 3,362,979. In the particularly preferred polyisocyanate mixtures containing higher nuclear polyisocyanates of the diphenylmethane series, the proportion of 2,4'-diisocyanato-diphenylmethane is also greater than about 20% by weight, based on the total mixture.

Component (b) includes any aliphatic, cycloaliphatic, aromatic, or heterocyclic compounds containing at least two epoxide groups, that is, 1,2-epoxide groups. The preferred polyepoxides used as component (b) have from about 2 to about 4 (preferably 2) epoxide groups per molecule and an epoxide equivalent weight of from about 90 to about 500 (preferably from 170 to 220). Examples of suitable polyepoxides include polyglycidyl ethers of polyvalent phenols such as pyrocatechol, resorcinol, hydroquinone, or 4,4'-dihydroxydiphenylmethane; of 4,4'-dihydroxy-3,3'-dimethyldiphenylmethane; of 4,4'-dihydroxy-diphenylmethane; of 4,4'-dihydroxydiphenylcyclohexane; of

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4,4'-dihydroxy-3,3'-dimethyldiphenylpropane; of 4,4'-dihydroxybiphenyl; of 4,4'-dihydroxydiphenylsulfone; of tris(4-hydroxyphenyl)methane; of the chlorination and bromination products of the above-mentioned diphenols; of novolaks (that is, reaction products of monovalent or polyvalent phenols and aldehydes, in particular formaldehyde, in the presence of acid catalysts); of diphenols obtained by the esterification of 2 moles of the sodium salt of an aromatic hydroxycarboxylic acid with one mole of a dihalogenoalkane or a dihalogenodialkyl ester (see British Patent 1,017,612); or of polyphenols obtained by the condensation of phenols with long chain halogenated paraffins containing at least two halogen atoms (see British Patent 1,024,288).

Also suitable are polyepoxide compounds based on aromatic amines and epichlorohydrin, such as N-di(2,3-epoxypropyl)aniline, N,N'-dimethyl-N,N'-diepoxypropyl-4,4-diamino-1-phenylmethane, and N,N'-diepoxypropyl-4-aminophenylglycidyl ether (see British Patents 772,830 and 816,923).

Suitable polyepoxides (b) also include glycidyl esters of polyvalent aromatic, aliphatic, and cycloaliphatic carboxylic acids. Examples of suitable glycidyl esters include phthalic acid diglycidyl ester, adipic acid diglycidyl ester, and glycidyl esters of reaction products of one mole of an aromatic or cycloaliphatic dicarboxylic acid anhydride and 1/2 mole of a diol or 1/n mole of a polyol containing n hydroxyl groups or hexahydrophthalic acid diglycidyl ester. The glycidyl esters can optionally be substituted with methyl groups.

Suitable polyepoxides (b) also include glycidyl ethers of polyhydric alcohols such as 1,4-butanediol, 1,4-butenediol, glycerol, trimethylolpropane, pentaerythritol, or polyethylene glycol; triglycidyl isocyanurate; N,N'-diepoxypropyloxamide; and polyglycidyl thioethers of polyvalent thiols such as bis(mercaptomethyl)benzene, diglycidyl trimethylene trisulfone; and polyglycidyl ethers based on hydantoins.

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Still other suitable polyepoxides include the epoxidation products of polyunsaturated compounds such as vegetable oils and their conversion products; the epoxidation products of di- and polyolefins, such as butadiene, vinyl cyclohexane, 1,5-cyclooctadiene, and 1,5,9-cyclododecatriene, and polymers and copolymers that retain epoxidizable double bonds, such as those based on polybutadiene, polyisoprene, butadiene-styrene copolymers, divinylbenzene, dicyclopentadiene, or unsaturated polyesters; epoxidation products of olefins obtainable by Diels-Alder addition reactions and subsequently converted into polyepoxides by epoxidation with peroxy compounds; and epoxidation products of compounds containing cyclopentene or cyclohexene rings linked together by bridging atoms or other bridging groups. Polymers of unsaturated monoepoxides, such as polymers of methacrylic acid glycidyl ester or of allyl glycidyl ether, are also suitable.

Preferred polyepoxide compounds for use as component (b) include polyglycidyl ethers of polyvalent phenols, in particular of bisphenol A; polyepoxide compounds based on aromatic amines, in particular bis(N-epoxypropyl)aniline, N,N'-dimethyl-N,N'-diepoxypropyl-4,4'-diaminodiphenylmethane, and N,N-diepoxypropyl-4-aminophenylglycidyl ether; polyglycidyl esters of cycloaliphatic dicarboxylic acids, in particular hexahydrophthalic acid diglycidyl ester, and polyepoxides of the reaction product of n moles of hexahydrophthalic acid anhydride and one mole of a polyol containing n-hydroxyl groups (wherein n is an integer from 2 to 6), in particular the reaction product of 3 mole of hexahydrophthalic acid anhydride and one mole of 1,1,1-trimethylolpropane, or 3,4-epoxycyclohexylmethane-3,4-epoxycyclohexane carboxylate. Mixtures of these compounds are, of course, also suitable.

Liquid polyepoxides or low viscosity diepoxides, such as bis(N-epoxypropyl)aniline or vinyl cyclohexane diepoxide, may in special cases further reduce the viscosity of already

liquid polyepoxides or convert solid polyepoxides into liquid mixtures.

5 Polyepoxide component (b) is used in a quantity corresponding to an equivalent ratio of isocyanate groups to epoxide groups of from about 1.2:1 to about 500:1 (preferably from 3:1 to 65:1, more preferably from 5:1 to 30:1).

10 Catalyst component (c) includes any mono- or polyfunctional organic amines containing tertiary amino groups. Suitable amines generally have a molecular weight of up to about 353 (preferably from 101 to 185). Tertiary amines that are liquid at the reaction temperature of the first reaction step are preferred. Examples of suitable or preferred amines include triethylamine, tributylamine, dimethylcyclohexylamine, N,N,N',N'-tetramethylethylene diamine, N,N-dimethylbenzylamine, 15 triethylenediamine, dimethyloctylamine, N-methylmorpholine, and bis(N,N-dimethylaminoethyl) ether. Suitable amines also include amines having a blowing action in addition to the catalytic action. A catalyst component (c) having a blowing action can also serve as blowing agent (e).

20 Catalysts (c) are used in a quantity of from about 0.01 to about 2% by weight (preferably from 0.01 to 0.1% by weight), based on the total weight of components (a) and (b).

Reaction stoppers (d) are poisons for catalysts (c). Suitable reaction stoppers include, for example, any esters of 25 organic sulfonic acids having an alkylating action. Preferred sulfonic acid alkyl esters have a molecular weight of from about 110 to about 250. Suitable organic sulfonic acid esters include aliphatic sulfonic acid alkyl esters, such as butane-sulfonic acid methyl ester, perfluorobutanesulfonic acid methyl ester, or hexanesulfonic acid ethyl ester, and aromatic sulfonic acid alkyl esters, such as benzenesulfonic acid methyl, ethyl, or butyl ester, p-toluenesulfonic acid methyl, ethyl or butyl ester, 1-naphthalenesulfonic acid methyl ester, 3-nitrobenzenesulfonic acid methyl ester, and 2-naphthalene-sulfonic acid methyl ester. The aromatic sulfonic acid esters

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mentioned above are preferred, with p-toluenesulfonic acid methyl ester being a particularly preferred component (d). Methyl iodide and dimethyl sulfate may also be used as component (d) but are less preferred.

5 Component (d) is used in a quantity at least equivalent to the tertiary amine nitrogen atoms of component (c).

10 Chemical blowing agents (e) used according to the invention may be water and/or phospholine oxide. Physical blowing agents (e) include hydrocarbons, such as pentane, butane, or hexane, and fluorochloro hydrocarbons.

15 Preferred catalysts (f) include not only the tertiary amines described above for component (c) but also any mixtures of the compounds such as exemplified above, a mixture of equal parts of pentamethyl diethylenetriamine, N-methyl-N'-(dimethylaminoethyl)piperazine, N,N-diethyl(ethanolamine), and silamorpholine being particularly preferred.

20 The preferred auxiliary agents and additives (g) include known foam stabilizers of the polyether siloxane type and mold release agents, such as polyamide waxes and/or stearic acid derivatives and/or natural waxes (such as carnauba wax).

25 The optional auxiliary agents and additives (g) include (g1) polymerizable olefinically unsaturated monomers used in quantities of up to 100% by weight (preferably up to 50% by weight), based on the total weight of components (a) and (b). Examples of additives (g1) include olefinically unsaturated monomers having no isocyanate-reactive hydrogen atoms, including diisobutylene; styrene; (C_1-C_4 alkyl)styrenes such as α -methylstyrene or α -butylstyrene; vinyl chloride; 30 vinyl acetate; maleimide derivatives such as bis(4-maleimido-phenyl)methane; acrylic acid (C_1-C_8 alkyl) esters such as acrylic acid methyl ester, acrylic acid butyl ester, or acrylic acid octyl ester, and the corresponding methacrylic acid esters; acrylonitrile; and diallyl phthalate. Any mixtures of such olefinically unsaturated monomers may also be used. If
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additives (g1) are used at all, styrene and/or (meth)acrylic acid (C_1 - C_4 alkyl) esters are preferred. When additives (g1) are used, conventional polymerization initiators such as benzoyl peroxide may also be used but are generally not necessary.

Other optional auxiliary agents and additives (g) include (g2) organic compounds in the molecular weight range of from about 62 to about 8000 containing at least 2 (preferably from 2 to 8 and more preferably 2 or 3) alcoholic hydroxyl groups, such as compounds known as starting components for polyurethanes. Examples of additives (g2) include simple polyhydric alcohols such as ethylene glycol, 1,6-hexanediol, glycerol, and trimethylolpropane; polyols containing dimethylsiloxane units, such as bis(dimethylhydroxymethylsilyl) ether; polyhydroxyl compounds containing ester groups, such as castor oil, or polyhydroxy polyesters of the type obtainable by the polycondensation of excess quantities of simple polyhydric alcohols of the type described above with carboxylic acids (preferably dibasic carboxylic acids) or their anhydrides, such as adipic acid, phthalic acid, or phthalic acid anhydride; and polyhydroxypolyethers obtainable by the chemical addition of alkylene oxides, such as propylene oxide and/or ethylene oxide, to starter molecules, such as water, the simple alcohols mentioned above, or amines containing at least two amine NH groups.

If used at all, the additives (g2) are used in a quantity corresponding to an NCO/OH equivalent ratio (based on the isocyanate groups of component (a) and the hydroxyl groups of component (g2)) of at least 2:1 (preferably not less than 2.5:1). The quantity of component (a) used must always be sufficient to ensure that the equivalent ratio of isocyanate groups of component (a) to the sum of epoxide groups of component (b), hydroxyl groups of optional component (g2), and any hydroxyl groups present in component (b) is at least 1.2:1 (most preferably from 4:1 to 30:1).

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It is generally not necessary to use auxiliary agents and additives (g1) or (g2). If used at all, additives (g1) are generally preferred to the compounds (g2), although both types could in principle be used together.

5 Further examples of optional auxiliary agents and additives (g) optionally used include (g3) fillers, such as quartz powder, chalk, microdol, aluminum oxide, silicon carbide, graphite, or corundum; pigments, such as titanium dioxide, iron oxide, and organic pigments (such as phthalocyanine pigments); plasticizers such as dioctylphthalate and tributyl or triphenyl phosphate; flame retardants, such as exolite or magnesium oxide; soluble dyes; and reinforcing materials, such as glass fibers or glass fabrics. Carbon fibers and carbon fiber fabrics and other organic polymer fibers, such as aramide fibers or liquid crystal ("LC") polymer fibers, are also suitable.

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Further examples of optional auxiliary agents and additives (g) include (g4) olefinically unsaturated monomers containing isocyanate reactive hydrogen atoms, such as hydroxyethyl methacrylate, hydroxypropyl methacrylate, and aminoethyl methacrylate.

20 The auxiliary agents and additives may be added to the starting materials (a) and (b) before the process of the invention is carried out or they may subsequently be added to the intermediate resin.

25 For carrying out the process according to the invention, the starting materials (a), (b), and (c) and optional auxiliary agents and additives (g) or a part thereof are mixed and allowed to react together in the temperature range of from about 20°C to about 150°C (preferably from 60°C to 130°C). After no more than 60% (preferably from 15 to 30%) of the isocyanate groups introduced into the starting mixture with component (a) have undergone reaction, the reaction is terminated by the addition of the reaction stopper (d).

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The intermediate product thus obtained is a storage-stable "B-state" material that is liquid at room temperature and may be used for the second step of the process of the invention, optionally after a storage time of essentially any desired length.

For this second step, the catalyst, the blowing agent, and, optionally, the other auxiliary agents and additives are added to the intermediate product and all the components are intimately mixed. The foamable mixture thus obtained is poured into either an open or a closed mold. The blowing process generally begins after the reaction mixture has been left in the mold for about 1 to 2 minutes and is generally completed after about 3 to 6 minutes. The foams obtained are tack-free after a total of about 6 to 12 minutes and the pores are finely divided and uniform. For obtaining optimum properties, it is frequently advisable to carry out an after-curing of the resulting resins at temperatures from about 120°C to about 250°C.

The foams of the invention can be used wherever heat resistance is needed, for example, as filling foam for electric insulation, for the production of structural materials for the construction of motor vehicles and aircraft, for the production of insulating boards, for use in engine rooms, and for the production of grinding discs (that is, as a supporting material for an abrasive).

The foams according to the invention are of low flammability and have low dielectric losses, excellent moisture and abrasion resistance, and excellent mold processing properties. The foamable mixtures of the invention can also be used for bonding various substrates, such as steel or copper plates, and plastics plates, such as plates of polybutylene terephthalate.

The following examples further illustrate details for the preparation of the compositions of this invention. The invention, which is set forth in the foregoing disclosure, is

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not to be limited either in spirit or scope by these examples. Those skilled in the art will readily understand that known variations of the conditions and processes of the following preparative procedures can be used to prepare these compositions. Unless otherwise noted, all temperatures are degrees Celsius and all percentages are percentages by weight.

EXAMPLES

Example 1

A mixture (800 parts by weight) of 60% 2,4'-diisocyanatodiphenylmethane and 40% 4,4'-diisocyanatodiphenylmethane (NCO content of 33.6%) was mixed at 50°C with 200 parts by weight of the diglycidylether of bisphenol A (epoxide number of 0.585) and 0.1 ml of dimethylbenzylamine. The resultant mixture was then heated to 120°C. The slightly exothermic reaction indicated the instantaneous onset of isocyanurate formation. The reaction mixture was cooled after a reaction time of 2 hours without external heating. The reaction temperature stabilized at about 90°C. A sample taken from the reaction mixture had an isocyanate content of 23% NCO. The reaction was terminated by the addition of 5 ml of stopping solution (15.4% by weight solution of p-toluenesulfonic acid methyl ester in a mixture of 60% 2,4'-diisocyanatodiphenylmethane and 40% 4,4'-diisocyanatodiphenylmethane. The reaction mixture was then stirred for a further 30 minutes at 120°C. A clear, yellow storage-stable resin, which was liquid at 20°C and had a viscosity of 2100 mPa·s at 25°C and an isocyanate content of 21%, was obtained ("Step 1").

Example 2

The reaction resin prepared according to Example 1 (100 parts by weight) was intimately mixed using a high speed stirrer with 1 part by weight of dibenzylmethylamine, 1 part by weight of a polyether polysiloxane (OS 20 foam Stabilisator BAYER AG) and 0.2 parts by weight of a 5% solution of phospholine oxide in tri-propylene glycol. The mixture was then poured into an open mold. Foam formation set in after a resting time of 6 minutes. The foam

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expanded uniformly and foaming was completed after 12 minutes. A solid, tack-free, open-celled rigid foam having a foam factor of 4.1 was obtained ("Step 2"). Foam factors are defined by the following equation:

5 **Foam factor =** $\frac{\text{Volume of foam}}{\text{Volume of starting mixture}}$

Example 3

10 The reaction resin prepared according to Example 1 (100 parts by weight) was intimately mixed for 3 minutes using a high speed stirrer with 1 part by weight of dimethylbenzylamine, 1 part by weight of polyether polysiloxane (OS 20), and 0.24 parts by weight of water. The mixture was then poured into a mold. The blowing reaction began at once and ended 15 after 3 minutes. The foam was tack-free after a further 3 minutes and was removed from the mold. The foam was finely divided and uniform and had a foam factor of 4.2 ("Step 2").

Example 4

20 The procedure was the same as described in Example 3 except that 100 parts by weight of glass powder were added to the reaction resin before the addition of water. The blowing reaction again set in immediately after the addition of water and intimate mixing of the components. Foaming was completed after 3 minutes and the foam was tack-free after a further 4 minutes. The finely divided, uniform rigid foam had a foam factor of 3.5 ("Step 2").

Example 5

30 The reaction resin prepared according to Example 1 (200 parts by weight) was intimately mixed with 2 parts by weight of a catalyst mixture and 1 part by weight of polyether polysiloxane. The catalyst mixture was a mixture of equal parts by weight of pentamethyl diethylenetriamine, N-methyl-N'-(dimethylaminoethyl)piperazine, N,N-diethylethanolamine, and silamorpholine and also functioned as the blowing agent. The

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mixture was allowed to stand at room temperature, and the foam factor and gross density were determined after the mixture had foamed and gelled (a total of 9 minutes) ("Step 2").

Gel time: 9 min

5 Foam factor: 4.2

Gross density: 142 (kg/m³)

The crude foam was cut into plates measuring 50 mm x 50 mm x 10 mm. The plates were tempered in a heating cupboard at 80°C, 120°C, and 160°C for 4 hours at each of these 10 temperatures and at 250°C for 5 hours. The compression resistances of these foam samples were then determined at the temperatures indicated below.

	Temperature (°C)	Compression resistance (N/mm ²)
15	23	0.90
	50	0.82
	100	0.81
20	150	0.91
	200	0.85

These results show that foams which are stable at high temperatures are obtained by this process.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A high temperature resistant foam prepared by a process comprising

(1) reacting a mixture of

- 5 (a) at least one organic polyisocyanate with
(b) at least one organic compound containing at least two epoxide groups in a quantity corresponding to an equivalent ratio of isocyanate groups to epoxide groups of from 1.2:1 to 500:1,

10 in the presence of

- (c) a tertiary amine as catalyst,
thereby forming an intermediate containing oxazolidinone and/or isocyanurate groups;

(2) terminating step (1) when no more than about 60% of the

- 15 isocyanate groups of component (a) have reacted by adding at least an equivalent amount, based on the tertiary amine catalyst (c), of

- (d) an alkylating sulfonic acid alkyl ester, methyl iodide, or dimethyl sulfate,

20 thereby forming a stable B-state intermediate having a viscosity of from 1500 to 20,000 mPa·s at 25°C; and

(3) converting said B-state intermediate to the high temperature resistant foam by adding

- (e) a chemical and/or physical blowing agent and

- 25 (f) a catalyst for accelerating reaction of isocyanate and epoxide groups.

2. A foam according to Claim 1 wherein in step (3) the chemical blowing agent is water and/or phospholine oxide, the physical blowing agent is a low boiling inert organic liquid, and the catalyst is tertiary amine.

3. A foam according to Claim 1 wherein one or more of components (a), (b), (c), (d), and (f) incorporates

- (g) auxiliary agents and additives.

4. A foam according to Claim 3 wherein the auxiliary agents and additives comprise up to 10% by weight,

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based on the total weight of components (a) and (b) excluding the amount of auxiliary or additive, of one or more foam stabilizers, mold release agents, or dyes, and up to 100% by weight, based on the total weight of components (a) and (b) excluding the amount of auxiliary or additive, of one or more inorganic fillers, organic fillers, olefinically unsaturated compounds, or organic compounds in the molecular weight range of from 62 to 8000 containing at least two alcoholic hydroxyl groups.

5 5. A foam according to Claim 4 wherein the olefinically unsaturated compound is styrene and/or a maleimide derivative.

10 6. A foam according to Claim 1 prepared by a process additionally comprising

5 (4) after-curing the foam at a temperature of from 120°C to 250°C.

0 7. A process for preparing a high temperature resistant foam comprising

5 (1) reacting a mixture of

0 (a) at least one organic polyisocyanate with

5 (b) at least one organic compound containing at least two epoxide groups in a quantity corresponding to an equivalent ratio of isocyanate groups to epoxide groups of from 1.2:1 to 500:1,

5 in the presence of

0 (c) a tertiary amine as catalyst,
 thereby forming an intermediate containing
 oxazolidinone and/or isocyanurate groups;

0 (2) terminating step (1) when no more than about 60% of the isocyanate groups of component (a) have reacted by adding at least an equivalent amount, based on the tertiary amine catalyst (c), of

5 (d) an alkylating sulfonic acid alkyl ester, methyl iodide, or dimethyl sulfate,

thereby forming a stable B-state intermediate having a viscosity of from 1500 to 20,000 mPa·s at 25°C; and

- 5 (3) converting said B-state intermediate to the high temperature resistant foam by adding
(e) a chemical and/or physical blowing agent and
(f) a catalyst for accelerating reaction of isocyanate and epoxide groups.

8. A process according to Claim 7 wherein in step
10 (3) the chemical blowing agent is water and/or phospholine oxide, the physical blowing agent is a low boiling inert organic liquid, and the catalyst is tertiary amine.

9. A process according to Claim 7 wherein one or more of components (a), (b), (c), (d), and (f) incorporates
15 (g) auxiliary agents and additives.

10. A process according to Claim 9 wherein the auxiliary agents and additives comprise up to 10% by weight, based on the total weight of components (a) and (b) excluding the amount of auxiliary or additive, of one or more foam stabilizers, mold release agents, or dyes, and up to 100% by weight, based on the total weight of components (a) and (b) excluding the amount of auxiliary or additive, of one or more inorganic fillers, organic fillers, olefinically unsaturated compounds, or organic compounds in the molecular weight range of from 62 to 8000 containing at least two alcoholic hydroxyl groups.

11. A foam according to Claim 10 wherein the olefinically unsaturated compound is styrene and/or a maleimide derivative.

12. A foam according to Claim 7 prepared by a process additionally comprising
30 (4) after-curing the foam at a temperature of from 120°C to 250°C.

13. In a method for preparing electric insulation, the improvement comprising using a foam according to Claim 1 as
35 a filling foam for said electric insulation.

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14. In a method for manufacturing structural materials for the construction of motor vehicles and aircraft, the improvement comprising using a foam according to Claim 1 as a filling foam for said structural material.
- 5 15. In a method for manufacturing insulating boards, the improvement comprising using a foam according to Claim 1 as a filling foam for said insulating boards.
- 10 16. In a method for producing grinding discs, the improvement comprising using a foam according to Claim 1 as a filling foam to support an abrasive in said grinding disks.

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